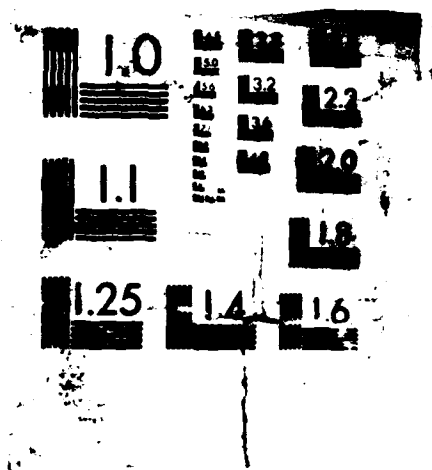AD-A183 976   A STRATEGY TO DETERMINE THE TRANSITION STATE OF AN   1/1
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A Strategy to Determine the Transition State
of an Electron Transfer Reaction

by

P. P. Schmidt and L. Blum

Oakland University
Department of Chemistry
Rochester, Michigan 48063

July 1987

A Strategy to Determine the Transition State of an

Electron Transfer Reaction

P. P. Schmidt

Department of Chemistry

Oakland University

Rochester, Michigan 48063

and

Lesser Blum

Department of Physics

University of Puerto Rico

Rio Piedras, Puerto Rico

Abstract

We suggest that the electron involved in an electron transfer reaction be represented as a wavepacket expanded in a limited basis set of appropriate functions. Saddle point optimization to determine the transition state involves moving the center-of-gravity of the wavepacket together with the atoms of the molecular framework.

Introduction

The theory of electron transfer between molecular or atomic fragments in polar solution, in biological milieu, and at electrodes has developed at the molecular level largely from the point of view of molecular orbital theory [1,2]. Thus, for example, one considers a transferable electron initially located at one atomic or molecular center. After successful transfer, the electron is located at a second, well-defined center. In the initial and final state, the state of the electron can be described in terms of local state functions: χ_i and χ_f. The effect of the solvent environment is represented as a collective degree of freedom and then separated from molecular electronic and vibrational degrees of freedom according to the precepts of the Born-Oppenheimer approximation. As one of us noted some time ago [2], when carried out carefully according to prescription, the Born-Oppenheimer-Holstein separation [3,4] applied to the electron transfer system yields a representation of the underlying electronic degrees of freedom which closely corresponds to the familiar Hartree-Fock-(Roothaan) [5] quantum mechanics of electrons. In essence, the transfer-electron occupies molecular orbitals of the reactive system in its initial and final states. This picture is most clearly stated in Hush's original formulation

[6]. The state of the electron can be specified in terms of a quantity λ which is used to mix the initial and final basis functions:

$$\Psi = N(\chi_1 + \lambda\chi_f) \tag{1}$$

and N is the normalization. Adjusting λ should fix the location of maximum density of electronic charge in the transition state. Indeed, this approach works and is successful within the context of the electron transfer theory as currently formulated.

Our objective, however, is ultimately to simulate electron transfer reactions in terms of the discrete structures of solute and solvent. One part of this plan is to consider saddle point optimization of individual configurations of particles. Another part of the plan is to incorporate the solute with its mobile electron in a Metropolis/Monte Carlo [7] simulation of the statistical transition state [8]. We found when we began this work that the conventional approach to the localization of the maximum density of migratory electronic charge was at best cumbersome and at worst impossible to use.

There is a considerable body of work on numerical optimization to determine the transition state as a saddle point [9-14]. In all instances in which these techniques are applied to reactions involving the transfer or rearrangement of atoms, an assumption of the adiabatic response of the electron is used. The migrating atom in a reaction behaves, for the purposes of the optimization, as a classical particle; it has a definite extent, i.e., it is not diffuse as is the electronic distribution. Thus, the saddle point can be located by the manipulation of definite points, the centers-of-mass of the atoms in the system.

This approach to the optimization of the location of the electron in the transition state of an *electron transfer reaction* is not easily extended with the usual molecular orbital view of the states of the electron. In

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principle, one could optimize λ of eq (1) together with the positions of the atoms, but this we found not to be the most direct and transparent method to use. Molecular orbital methods are ideally suited to the determination of stable, stationary states of molecular systems, states which are characterized by substantial accumulations of electronic charge in the vicinities of the atoms which make up the molecule. Thus, molecular orbital theory is not the optimum representation to use to describe the non-stationary transition state.

On the other hand, for the transition state of the electron transfer reaction, we propose, first, that the electronic substructure of the reactants be handled in the usual manner, in terms of the molecular orbital theory. However, second, the migratory electron, should be handled as a wavepacket which is in turn expanded in a set of basis functions sufficiently large to give an accurate value of the energy of the transition state. The center-of-gravity of the wavepacket can be manipulated together with the locations of the atoms of the substrate in order to locate the transition state. The wavepacket is used in the much same spirit as Heller's [15] use of the semiclassical Gaussian wavepacket in scattering.

Method and Example

We illustrate our proposal for determining the transition state of the electron transfer reaction with a simple model system. With reference to Fig. 1, consider two atomic centers, A and B, separated by a distance R_{AB}. We allow variable charges on the cores of A and B, up to two positive charges, and a complement of valence level electrons, maximum of two. The valence level electrons occupy simple molecular orbitals of the combined A and B reactant system. Finally, the migratory transfer electron is handled

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as a wavepacket, as indicated, expanded in a basis set which consists of 1s, 2s, and three 2p Slater functions expanded in GTO's [16].

The model system is summarized in Fig. 1 as follows. The underlying electronic charge distribution which arises from the interaction of the A and B species is indicated by the light dotted lines. These lines schematically outline the regions of electronic charge accumulation. The transfer electronic charge is indicated by the bolder dashed line. The origin of this distribution, O in the figure, lies in the space of the AB system. In a saddle point calculation, the origin O would be optimized along with the surrounding atoms to their locations in the transition state.

We assume a closed shell or isolated valence electron system. Therefore, we ignore the exchange interactions which operate between the migratory and the underlying electrons. These interactions certainly may be important in many instances, but for this initial report, we believe it is more important to stress the major features of the model.

The core electrons are modelled simply as a single GTO; this yields an electronic charge density about the atoms A and B of the type

$$\rho(r) = \frac{Z^- e}{\pi^{3/2} \delta^3} \exp(-r^2/\delta^2) \tag{2}$$

In addition, of course, there is an overlap charge density of a similar form.

It is worth noting that the model system we use can represent both intra- and inter-molecular transfer. For non-bonding, intermolecular transfer, the electronic overlap distribution is vanishingly small. The height of the barrier to transfer in this case is essentially the difference between the energy of the free (or pseudosolvated) and bonded electron. On the other hand, there are examples of intramolecular electron transfer, such as the case of the heptafulvalene radical anion [17], for which the

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interaction of the transfer electron with the overlap charge densities
should contribute importantly to the height of the barrier.

Results

Several calculations were carried out. The center-of-gravity of the
transfer electron wavepacket was moved along the AB-line; we calculated
energies on the AB line as there was no solvent present to warrant
optimization off the line. It is clear, however, that if solvent is
present, optimization will yield locations for the center-of-gravity of the
wavepacket off the AB line.

The results of our calculations are summarized in the Figs. 2 through
5. The simplicity of the model, the absence of exchange interactions,
precludes an antibonding state for the transfer electron for all
separations. Thus, it is possible to choose combinations of core positive
and valence electronic charge and values for the AB separation which yield
energy minima for the transfer electron. Such minima may persist even in
presence of exchange interactions.

Fig. 2 illustrates the energy of the wavepacket moving in a fixed field
of two core atoms held at a distance of 1.2Å apart. Each atom is
electrically neutral at infinite separation. At this close separation, the
system exhibits energy minimum for the electron; however, the electron-
electron repulsion at each atom forces the transfer electron into the space
between the atoms as being energetically the most stable. Note, there is a
barrier to the penetration of the electron into the atomic core. The
reaction of Figs. 2 and 3 corresponds to one of the type

$$A^- + A \underset{\longleftarrow}{\longrightarrow} A + A^-. \tag{A}$$

Figure 3, in contrast to Fig. 2, shows the behavior of the transfer

electron in the field of the same two atoms, but here the fixed distance is

2.5Å. There is an attraction of the electron to the atom--an electron

affinity to form an anion, but very little penetration to the core. The

depression of the energy at the center reflects the tendency of the energy

to go to a zero value as the interaction with the surroundings vanishes with

large distance.

Figs. 4 and 5 represent reactions of the type

$$A^+ + A \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; A + A^+ \tag{B}$$

and

$$A^+ + B \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; A + B^+ \tag{C}$$

respectively. The only distinction between these two reactions is the fact

that for the heteronuclear reaction, the parameters δ_a and δ_b differ by

0.1Å. It is clear, however, in both cases that there is a barrier to the

migration of the electron from one center to the other.

Discussion

We have found only energy maxima with reference to the electron

interacting with molecular surroundings. We have not yet determined that

the overall system--atom-atom interactions as well as atom-electron

interactions--is a saddle point. It is entirely possible that in a

reaction, especially in a reaction in solution, the electron is carried

along from its initial to final state in a local energy well while the whole

system always has at least one mechanically unstable degree of freedom. The

role of the solvent may be partially to solvate the migratory electron. The

electron in the transition state in essence would be trapped between

reactive centers and molecules of solvent. If this should be the case in

some instances, some of what has been learned about solvated electrons ought

to apply to the intramolecular, solvated electron transfer reaction [18].
On the other hand, in those instances for which there is a clear energy
barrier in the transition state, tunnelling of the electron will be
necessary to get it to the final state. Here then, the well-developed
machinery of the diabatic transition state theory should apply [1].

For the past 30 years, the electron transfer theory has used polar
dielectric solvent model as an integral part; the outer sphere solvent is
usually handled in varying degrees of sophistication and complexity as a
polar continuum [1]. Although local molecular vibrations are frequently
included in the analyses, they are generally examined in the harmonic limit
with the machinery of the normal mode analysis. The overall accuracy of
the theoretical account of observed electron transfer is a matter of growing
concern [19].

It is possible that the dependence of the electron transfer reaction on
local vibrational degrees of freedom may be stronger than the dependence on
the continuum dielectric response. There is the well-known example of the
solvent independence of the radiationless transition in benzene [20]. Energy
loss to vibrational modes is known to involve the C-H stretch motions; there
is only a very weak dependence on solvent. Such a marked insensitivity to
the solvent may not apply in general to electron transfer, redox reactions;
it is somewhat early to tell. However, the growing difficulty in getting
agreement between experiment and theory for a number of reactions in
several solvents points to a more important involvement of local vibrational
modes. The role of the outer modes will not disappear, of course. Their
influence can be incorporated into the local vibrational degrees of freedom
as mode dressing through renormalization [21]. A focus of attention on the
local modes may redress the strong emphasis the current theory places on the
outer sphere degrees of freedom. The strategy for determining transition

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states which we have proposed we believe is well suited to exploring this issue.

Our purpose, as set forth in this note, was a modest one, to indicate that it is possible to determine transition states for electron transfer reactions by manipulating the center-of-gravity of the mobile electronic charge density. We have not included an account of exchange interactions or configuration interactions. These interactions are important, and will be considered in due course. In spite of the implicit computational costliness of the approach we advocate, we believe nevertheless that it may provide a way to carry out useful simulations of the electron transfer reaction.

Table 1

Parameters used in the calculations:

A. Slater basis functions[a,b]:

$\zeta_{1s} = 1.0 \qquad \zeta_{2s} = 2.0$

B. Primitive Gaussian atomic orbital[c]:

$\delta_A = \delta_B = 0.5$ (Figs. 2-4): $\delta_A = 0.4$, $\delta_B = 0.5$ (Fig. 5)

C. Charges and interatomic distances, as indicated in the figures.

_____

Slater functions in terms of a scaled Gaussians [16] (t = term symbol):

$$\psi_{1t}(r) = \zeta^{3/2} \gamma_{1t}(1, \zeta r)$$

Guassians (cf. ref. 16):

a. $\gamma_{ns}(1, r) = (2/\pi)^{3/4} \sum_{i=1}^{6} d_{ns,i} \alpha_{ni}^{3/4} \exp(-\alpha_{ns} r^2)$

$(n = 1, 2)$

b. $\gamma_{2p_z}(1,r) = 2(2/\pi)^{3/4} z \sum_{i=1}^{6} d_{2p,i} \alpha_{2i}^{5/4} \exp(-\alpha_{2i} r^2)$

c. Primitive Gaussian atomic orbital:

$$\gamma_{1s}(r) = \frac{1}{\pi^{3/4} \delta^{3/2}} \exp(-r^2/2\delta^2)$$

Figure Captions

1. A schematic representation of the charge transfer system. The atomic cores are labelled A and B and are located on the z-axis. The extent of the underlying valence electronic charge is indicated by the dotted lines. The bold dashed line indicates the extent of the transfer-electron wavepacket.

2. The energy of the transfer electron in the field of two neutral atoms A: the reaction is $A^- + A \rightarrow A + A^-$. The separation between the A-atoms is 1.2 Å.

3. The same system as in Fig. 2. The interatomic distance is 2.5 Å.

4. The energy of the electron in the field of two identical cations: reaction; $A^+ + A \rightarrow A + A^+$. The interatomic separation is 1.5 Å. The height of the barrier increases with increasing A-A separation.

5. The energy of the electron in the field of two dissimilar cations A and B: reaction; $A^+ + B \rightarrow A + B^+$. Here $\delta_a - 0.4$ Å and $\delta_b - 0.5$ Å. The interatomic separation is 1.5 Å.

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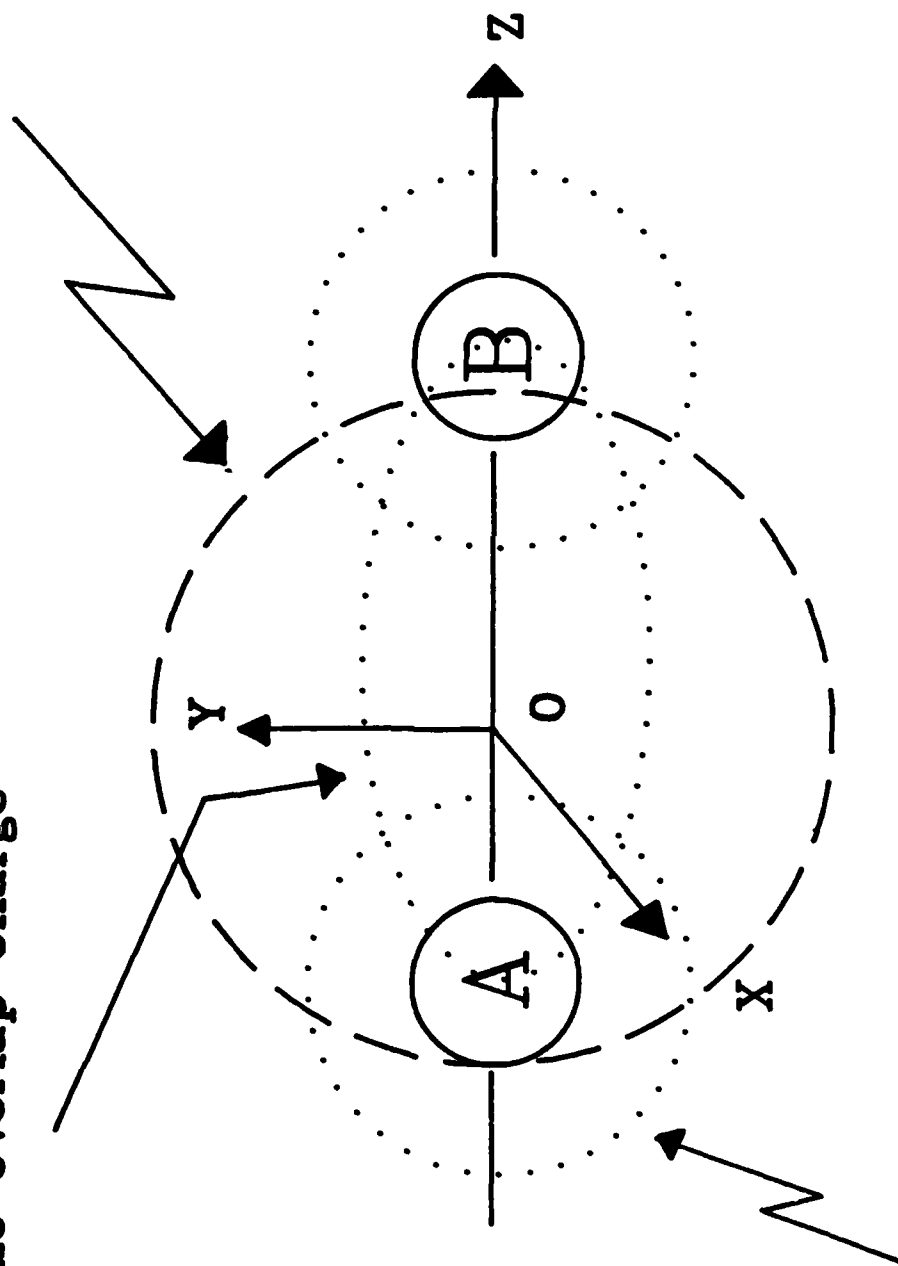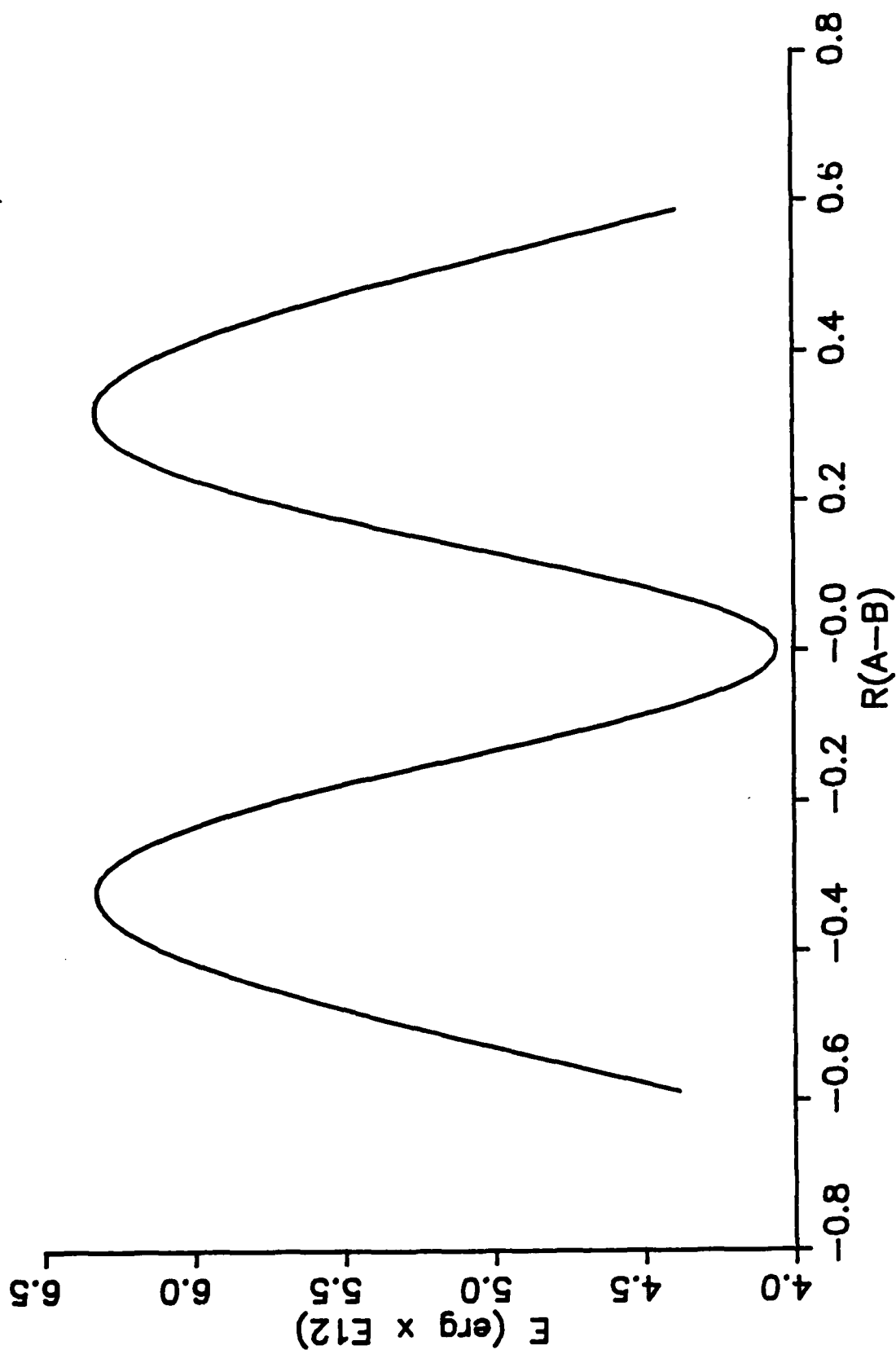19. J. T. Hupp and M. J. Weaver, J. Phys. Chem., 89 (1985) 1601; T.

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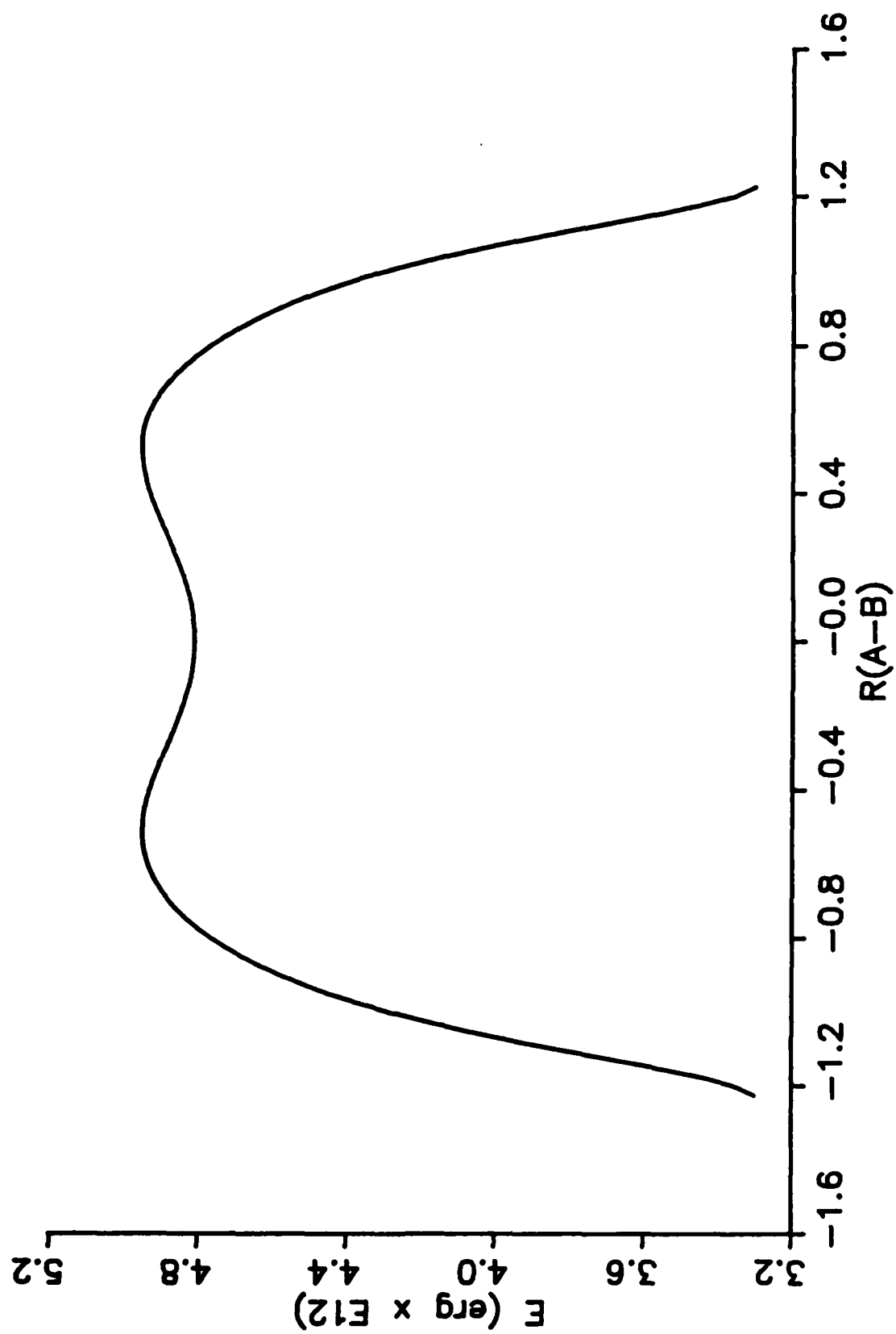21. P. P. Schmidt, Z. Naturforsch., 29a (1974) 880

Transfer Electron

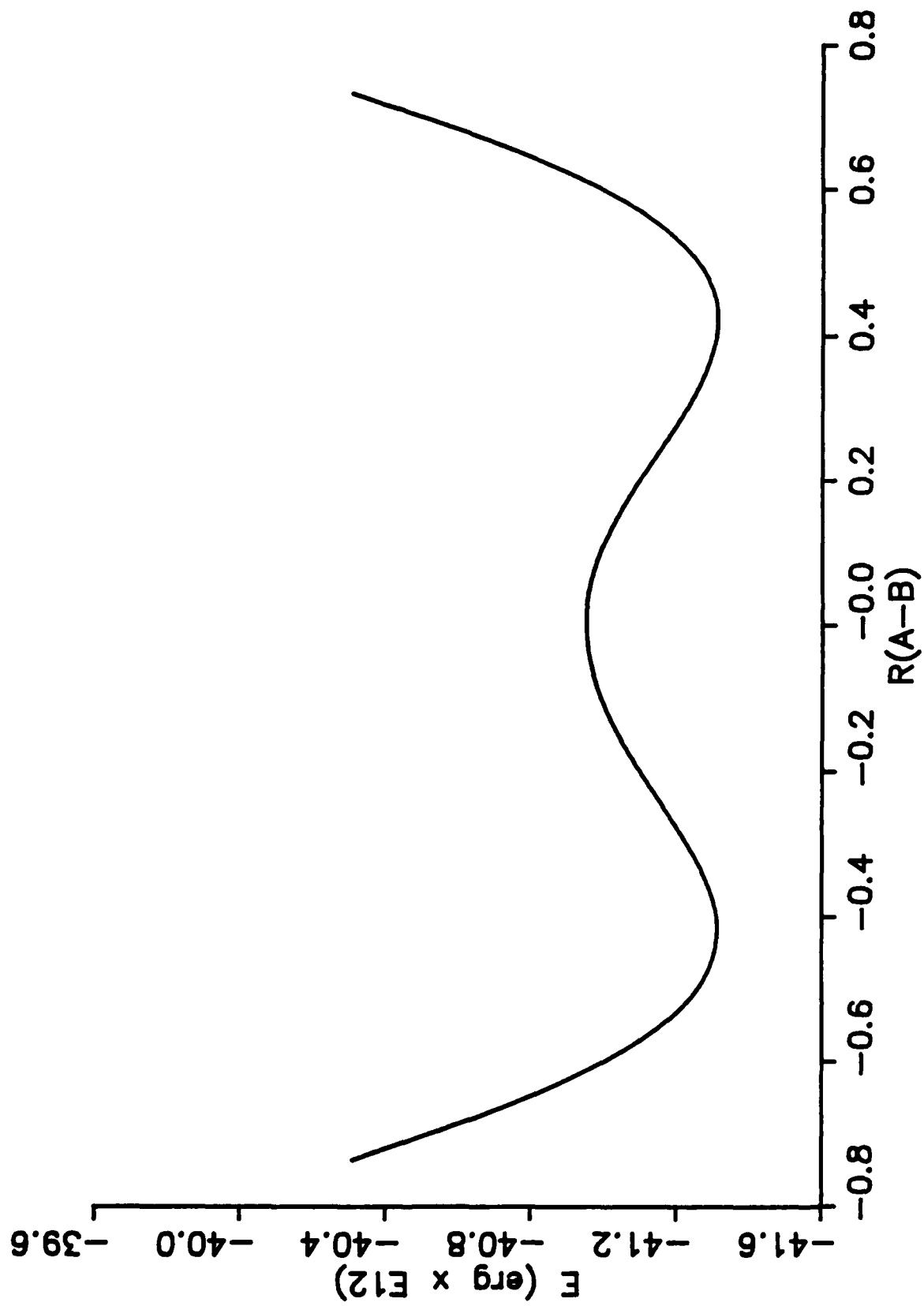Electronic Overlap Charge

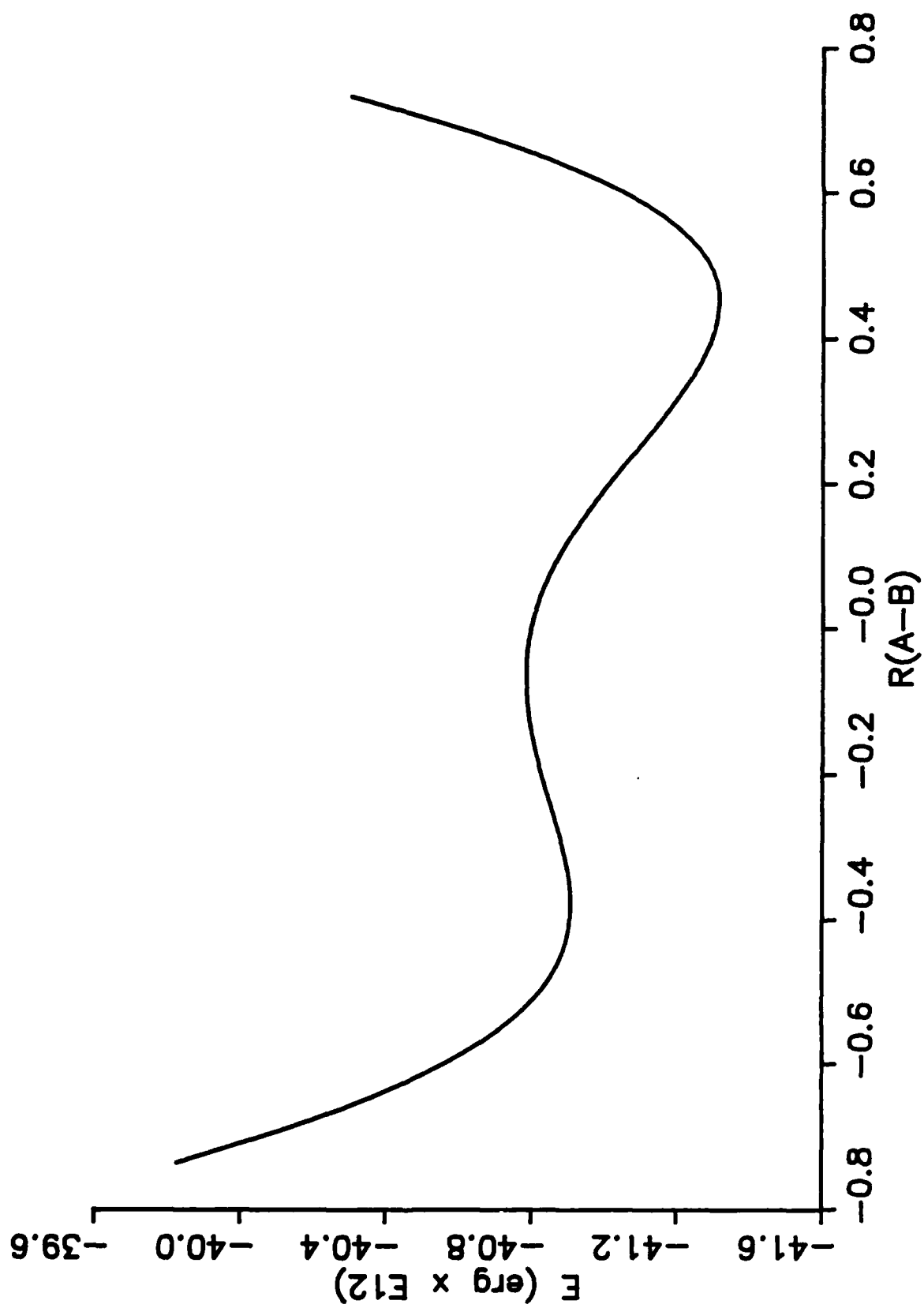Core Electron

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